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Degradation Studies on LiFePO_4 cathode

Wednesday, 8 October 2014

Expo Center, 1st Floor, Center and Right Foyers (Moon Palace Resort)

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Lithium-ion batteries are a promising technology for automotive application, but limited performance and lifetime is still a big issue. The aim of this work is to study and address degradation processes which affect LiFePO_4 (LFP) cathodes - one of the most common cathodes in commercial Li-ion batteries.

In order to evaluate how the LFP cathode is affected by C-rate a LFP working electrode, Lithium metal foil counter electrode and Lithium metal reference electrode was tested in a 3-electrode setup with a standard 1M LiPF_6 in 1:1 EC/DMC electrolyte and glass fiber separator. The working electrode/counter electrode was subjected to several charge/discharge cycles between 3.0 V and 4.0 V at different discharge rates. Figure 1 shows the voltage profile of the LFP electrode (solid line) and full battery (dotted line) during charge/discharge process. It is seen that the higher the C-rate, the higher is the polarization furnished by the counter electrode which reduces the capacity.

In Figure 2, the discharge capacity [mAh/g] is plotted vs the number of charge/discharge cycles. Series of 10 cycles at a given C-rate was applied to the battery. Each series was followed by a C/10 cycle (green points). A linear fit has been applied to the first series (omitting first two cycles where instability of the system is observed), in order to calculate the degradation rates.

High C-rates are seen to affect the discharge capacity, but the capacity is almost completely recovered (green points) and only a limited degradation occurs.

Impedance spectroscopy has been also applied to investigate the LFP cathode degradation. Figure 3 shows the imaginary part of the impedance measured at 50% State-of-Charge after each series of cycles. The relative increase in the impedance arc around 1 KHz (assumed to be associated with charge transfer resistance at the LFP particle surfaces) is seen to gradually decrease with increasing number of series. This indicates that more cycles per series is needed to establish a convincing relation between C-rate and degradation.

The degradation studies will be coupled with **FIB/SEM** analysis in order to observe changes in the pore structure or micro cracks that would affect electronic percolation. Figure 4 displays an example of a fresh LFP cathode after FIB cutting. White particles are LFP grains while the black area contains carbon particles and pores, which are difficult to distinguish from each other. Substitution of the epoxy resin with a silicon resin increases the contrast between pores and carbon particles [1] and this will be used in the forthcoming FIB/SEM analysis.

References

[1] M. Ender et al, *Journal of The Electrochemical Society*, **159** (7) A972-A980 (2012)

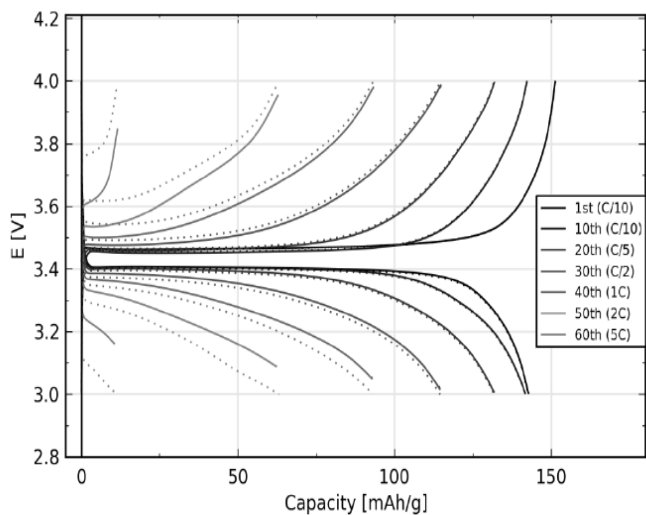


Figure 1. Charge-Discharge curves of LiFePO_4 cathode (solid line) and full battery (dotted line) at different C-rate

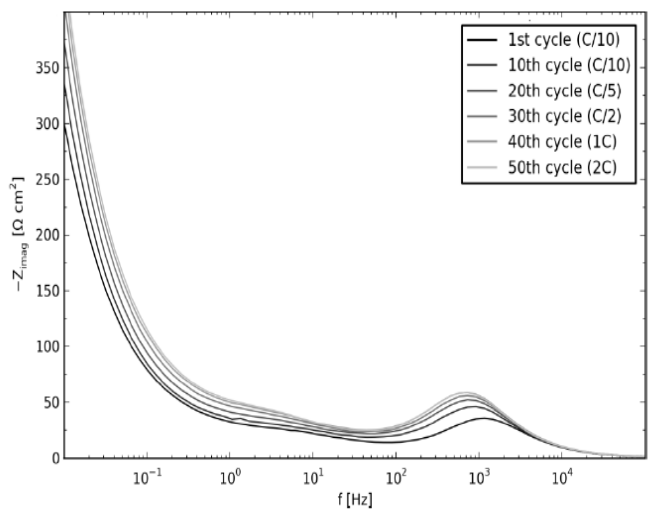


Figure 3. Bode plot of the imaginary part of the LFP impedance measured at 50% SOC after each series of cycles

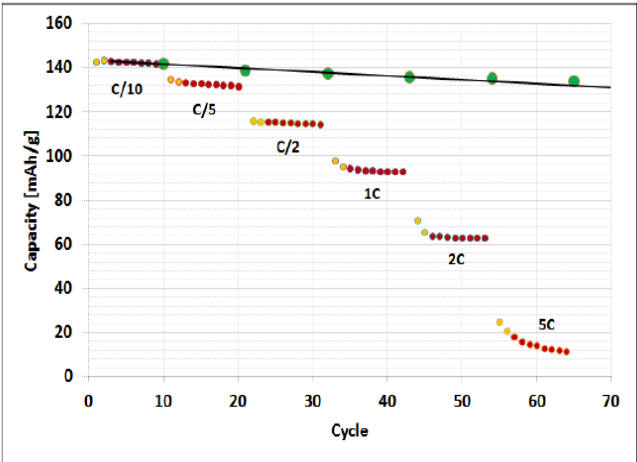


Figure 2. Capacity fading vs cycle number.

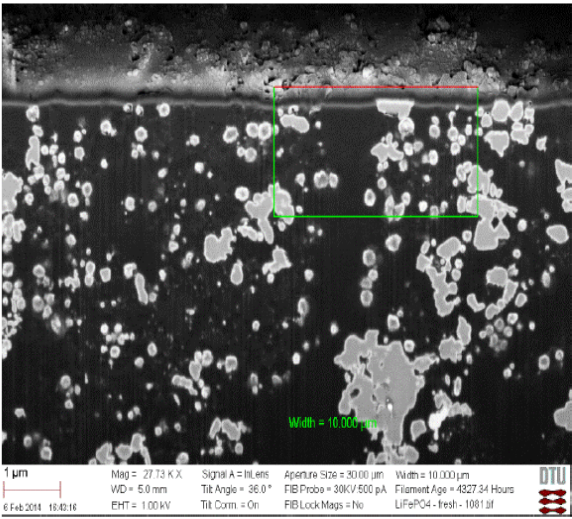


Figure 4. SEM image of the LiFePO_4 electrode after FIB cutting.